

Numerical Simulation of NO Formation in Methane, Methanol and Methyl Formate in a Homogeneous System

J. K. Tanui and P. N. Kioni

Abstract—In this study, methane/air, methanol/air, and methyl formate/air stoichiometric mixtures have been numerically simulated at constant volume, low pressure of 2.7 atm, and temperature ranging from 1000 K to 1950 K with an aim to establish the impact of fuel oxygenation on NO formation. These conditions represent those behind a reflected shock in a shock tube, which is modeled as adiabatic homogeneous mixture with constant internal energy and constant volume. Various chemical kinetic mechanisms have been employed and extensively tested so as to ensure validity of the results. A comparison of NO profiles and other radicals- CH, HCN, N, and N₂- that are dominant in its formation have been done. Since the initial temperatures are high, the flame temperatures attained by all the mixtures are also high; from approximately 2800 to 3100 K for initial temperatures of 1000 and 1950 K respectively. Therefore, NO are formed mostly through thermal NO mechanism with prompt NO being less significant. It has been observed that at very high temperatures the difference in N and NO formation in the three fuels is not very significant (same order of magnitude) as compared to that observed in relatively low temperatures attained by freely propagating and diffusion flames. At high temperatures the major rate-limiting steps for NO formation, involving high activation energy are $N_2 + O \rightarrow NO + N$ (318.4 KJ/mol), $CH_2 + N_2 \rightarrow HCN + NH$ (309.69 KJ/mol) and $N_2 + C \rightarrow CN + N$ (187.90 KJ/mol).

Keywords—Homogeneous mixture; methane; methanol; methyl formate; NO

I. INTRODUCTION

A high level of exhaust nitrogen oxides (NO_x) emissions from automobiles forms photochemical smogs in the environment when reacted with hydrocarbon. With the increasing use of biofuels, there is need to established their contribution of NO_x emissions into environment. A typical biodiesel fuel has C14-C18 fatty acid methyl esters; methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate in different compositions. The chemical kinetics of these large carbon chain esters are complex. Their combustion processes contain hundreds to thousands of intermediate compounds thus making computation difficult. To tackle this problem, researchers have been using a surrogate fuel (both single and multi-component) to represent a real fuel. In this study, we have particularly considered methyl formate (simplest methyl ester molecule) to represent a biodiesel fuel. The choice has been due to its simple structure. Even though methyl formate

does not have a high molecular weight as a real biodiesel fuel, it has the essential chemical structural features of an ester.

The chemical kinetics of methyl formate have recently been studied by Dooley *et al* [1] [2]. The mechanism developed [2] has been validated in a wide range of conditions, viz, a variable pressure flow reactor, shock tube facility and outwardly propagating flames. In a later investigation [1], Dooley *et al.* studied a series of burner stabilized flames at pressures of 22-30 Torr and equivalence ratios from 1.0 to 1.8 for flame conditions of 25-35% fuel to further validate their chemical kinetic reaction mechanism. To our knowledge, NO formation pathways for methyl formate flames have never been reported. With the earlier reports [3] [4] that NO_x formation in biodiesel fuel are higher than those of fossil fuel, it is important to understand how the NO formation is affected by oxygenation in the fuel.

This study reports on the comparison of NO formation in methane/air, methanol/air, and methyl formate/air stoichiometric mixtures in a homogeneous system. The investigation has been done for mixtures at pressure of 2.7 atm and temperature ranging from 1000 to 1950 K. Various chemical kinetic mechanisms have been employed for the different fuels. Methane and methanol flames are computed using GRI-Mech 3.0 reaction mechanism [5], while methyl formate flame is computed by combining the Dooley *et al* [2] oxidation mechanism with the Leeds NO_x oxidation mechanism [6]. All mechanisms used in this study have been widely validated and tested. GRI-Mech 3.0 reaction mechanism has been validated and tested in previous investigations [7], [8]. Dooley *et al.* oxidation mechanism has also been validated in a wide range of conditions as mentioned in the preceding paragraph. Similarly, Leeds NO_x oxidation mechanism has been validated in flow reactors, perfectly stirred reactors and low pressure laminar flames by Hughes *et al.* [9].

II. NUMERICAL MODEL

The experimental conditions behind a reflected shock in a shock tube can be modeled as a adiabatic homogeneous mixture with constant internal energy and constant volume. In this numerical computation, methane/air, methanol/air, and methyl formate/air mixtures have been studied at constant volume of 200 cm³, low pressure of 2.7 atm, and temperature ranging from 1000 K to 1950 K. The governing equations for this configuration are single point transient (zero-dimensional

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time dependent), which are given as

$$\rho \frac{\partial Y_i}{\partial t} = w_i \quad i = 1, \dots, N, \quad (1)$$

$$\rho C_v \frac{\partial T}{\partial t} = - \sum_{i=1}^N u_i w_i + \frac{Q}{V}, \quad (2)$$

$$p = \rho RT \sum_{i=1}^N (Y_i / W_i). \quad (3)$$

Here, ρ is density, t is time, C_v is specific heat capacity at constant volume, p is pressure, R is universal gas constant, T is temperature, N is total number of species, V is reactor volume, Q is rate at which heat is transferred across the reactor, while u_i , w_i , Y_i and W_i represent internal energy, rate of production by chemical reactions, mass fraction and molecular weight of species i .

The flames are numerically simulated using the RUN1DL code in the software package COSILAB [10]. Conservation equations are discretized with finite difference method. Both central and one-sided difference (upwind) schemes are adopted in the discretization of first-order derivatives. The time dependent version of the governing equations are first integrated with respect to time in steps starting with initial specified profiles, which should satisfy the equations at time level $m=0$ with $t=t^0 \equiv 0$. The solutions to governing equations are then sought at the subsequent time levels ($m = 1; t = t^1$), ($m = 2; t = t^2$), ..., with $0 = t^0 < t^1 < t^2 < \dots < t^m < \dots$, where the superscript m is used to identify quantities at time level m . The integration is complete when either a specified time level m_{max} or time t_{max} is reached. The thermodynamic properties for the species, which are in CHEMKIN format are obtained from Princeton University kinetic model databases [11] and GRI-Mech 3.0 databases [5].

III. RESULTS AND DISCUSSION

A comparison for ignition delay times for the gas mixtures is shown in Fig. 1. The shock tube ignition delay times for these fuels have been done separately under various conditions by different researchers [2], [12]–[15]. The simulations for ignition delay times for these fuels have been repeated to check their differences. Under all the temperatures tested, methane have higher ignition delay times as compared to methanol and methyl formate. The plot reveal a trend of reduction of ignition delay time with increase in fuel oxygenation.

Figures 3-9 show the species concentration profiles for NO and other minor species related to its formation. Methane/air mixture has a significantly higher concentration (a difference of one order of magnitude) profiles of immediate precursor species - CH and HCN- for prompt NO formation. Then, a significantly higher NO forming in methane than the oxygenated fuels will be expected, however, this is not the case. A slight difference is seen in the NO concentration profiles for the three flames. This then means NO is formed mostly through the high temperature thermal NO reactions, since the temperatures are quite high (up to a maximum of approximately 2900 K as shown in Fig 2). The reaction between nitrogen molecule

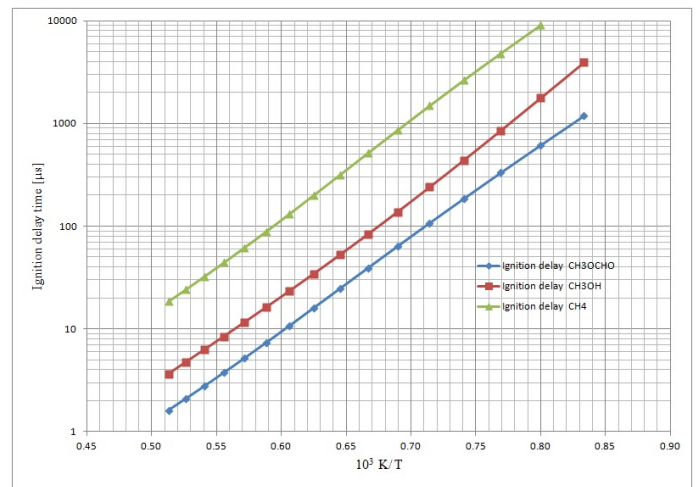


Fig. 1. Ignition delay times for methane/air, methanol/air and methyl formate/air mixtures at pressure of 2.7 atm

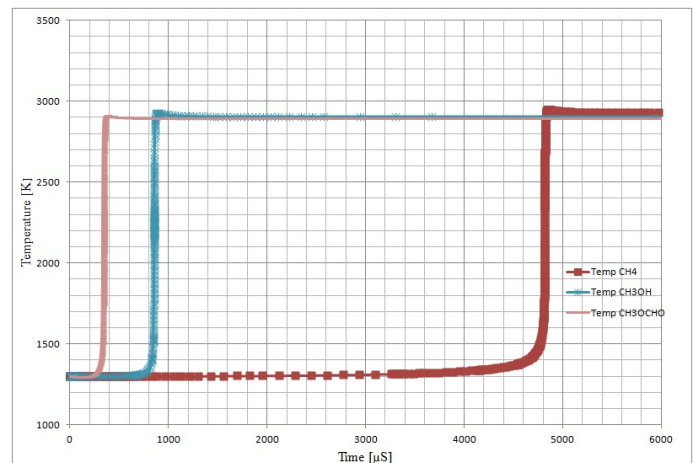


Fig. 2. Temperature profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

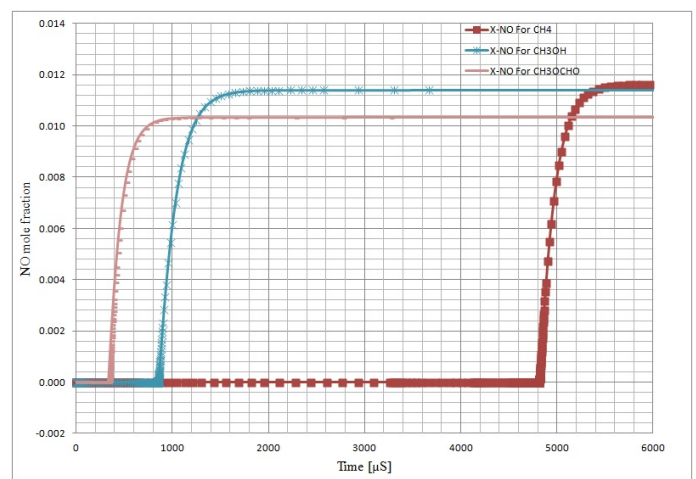


Fig. 3. NO concentration profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

and oxygen atom in Zeldovich mechanism: $N_2 + O \rightarrow NO + N$ has a high activation energy, for instance a value of -

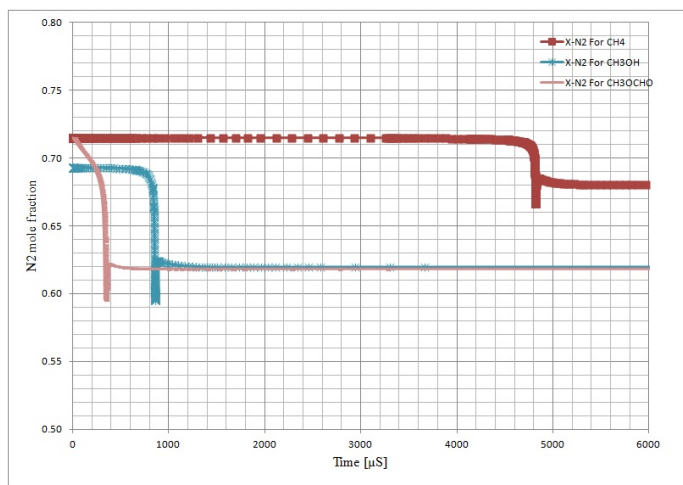


Fig. 4. N₂ concentration profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

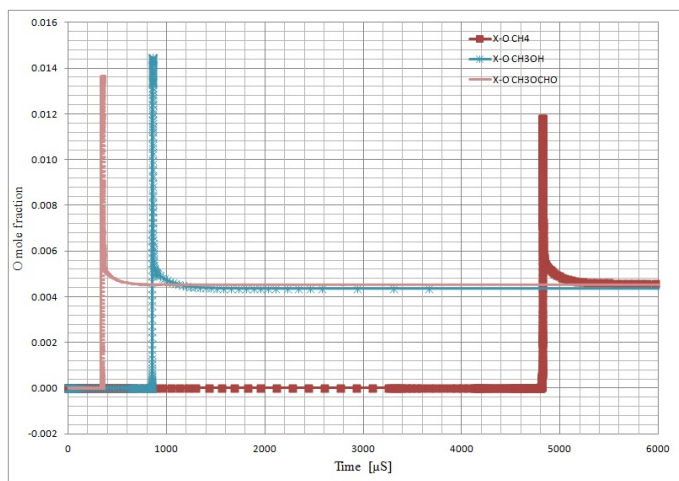


Fig. 7. O concentration profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

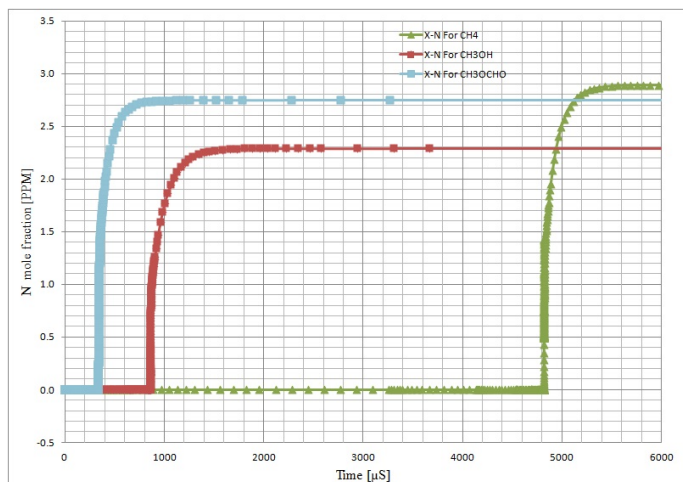


Fig. 5. N concentration profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

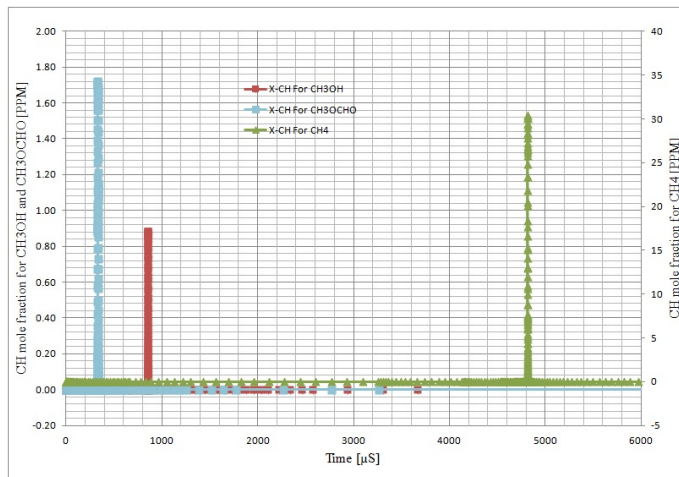


Fig. 8. CH concentration profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

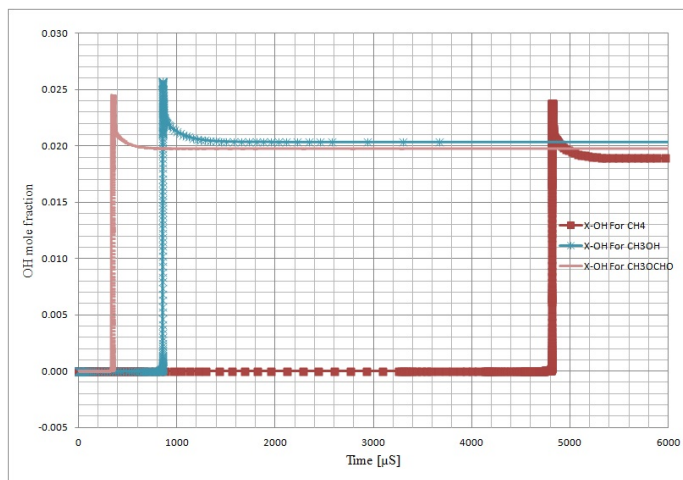


Fig. 6. OH concentration profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

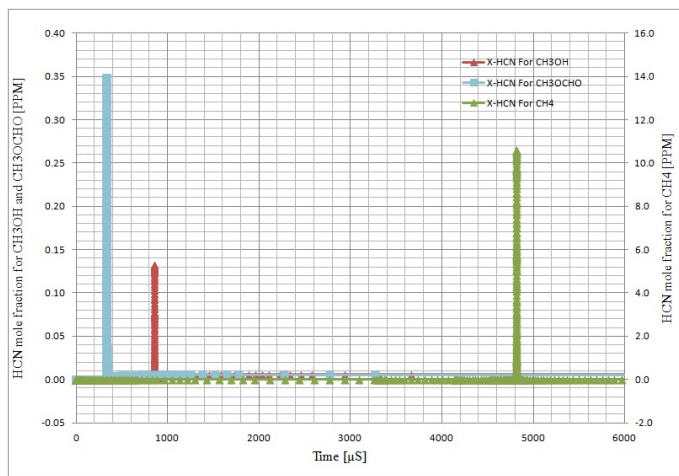


Fig. 9. HCN concentration profiles for the three mixtures at temperature of 1300 K and pressure of 2.7 atm

318.4 KJ/mol in Leeds NO_x oxidation mechanism. Therefore, the reaction proceed sufficiently fast at high temperatures and

hence it is the rate-limiting step for NO formation. Other reactions with high activation energy which involve nitrogen

molecule and other radicals are $\text{CH}_2 + \text{N}_2 \rightarrow \text{HCN} + \text{NH}$ (309.69 KJ/mol) and $\text{N}_2 + \text{C} \rightarrow \text{CN} + \text{N}$ (187.90 KJ/mol). All these reactions have high activation energy because of the stable N_2 triple bond. The influence of these reactions in NO formation is clearly seen in the freely propagating and diffusion flames, which have three order of magnitude reduction of NO formed due to low temperature attained in the flame. The observation of N atom profile concentration being within the same order of magnitude for the three mixtures as opposed to those observed in freely propagating and diffusion flames is also explained by these high activation energy reactions. At low temperatures, N formation route is initiated through the reaction: $\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N}$, while at high temperatures N is formed through both this reaction and the high activation energy reactions mentioned before.

The plots of NO concentration profiles for the three fuels mixtures at different temperatures, Figs. 10 and 11, reveal a similar trend. The rate of increase of NO concentration with temperature is proportional in the three fuels. This trend is expected because as initial temperature is increased, the final temperature attained by mixture is also increased.

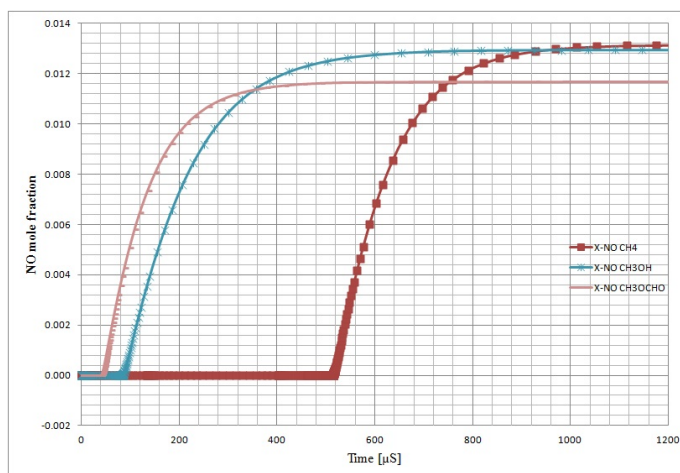


Fig. 10. NO concentration profiles for all mixtures at temperature of 1500 K and pressure of 2.7 atm

IV. CONCLUSION

NO formations in methane/air, methanol/air, and methyl formate/air stoichiometric mixtures in a homogeneous system have been investigated in this study. The NO concentration profiles for the three mixtures exhibit small differences in terms of magnitude. It has been established that NO formation in high temperatures is mostly through thermal NO reactions by Zeldovich mechanism. The rate-limiting step in the Zeldovich mechanism: $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ is the decisive reaction for NO formation at high temperature. The availability of the O atoms and nitrogen molecules in all three fuels considered result in a similar amount of NO formed. The small difference observed in the production of NO is attributed to the different maximum temperatures attained by these mixtures and the prompt NO formation. It has also been established that at high temperatures, N formation route is different from that

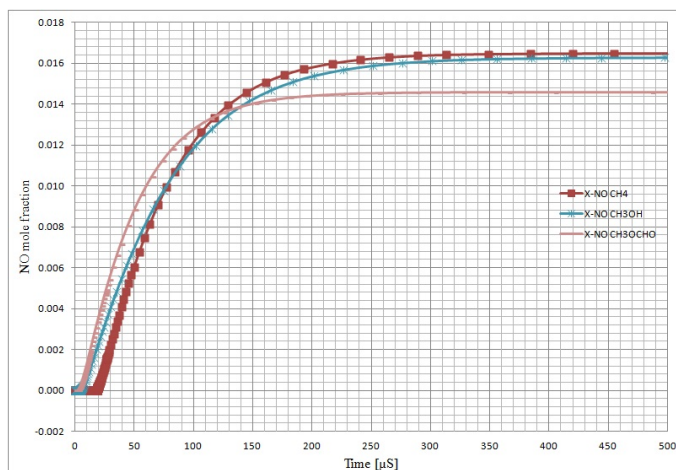


Fig. 11. NO concentration profiles for all mixtures at temperature of 1950 K and pressure of 2.7 atm

at low temperatures. At high temperatures the rate-limiting steps: $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ (318.4 KJ/mol), $\text{CH}_2 + \text{N}_2 \rightarrow \text{HCN} + \text{NH}$ (309.69 KJ/mol) and $\text{N}_2 + \text{C} \rightarrow \text{CN} + \text{N}$ (187.90 KJ/mol) involving high activation energy dictate its formation. Hence, a small difference (within the same order of magnitude) is observed in the N concentration profiles in these mixtures as compared to those for freely propagating and diffusion flames which attained relatively low temperatures.

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